

REPLACEMENT OF CHROMATES IN PAINTS AND CORROSION
PROTECTION SYSTEMS

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16. Abstract <p>This technical report presents the second stage results of a multi-year project to develop chromate-free paints and corrosion protection systems. Chromate-containing coatings and paints are very effective in providing corrosion resistance and are widely used in the manufacturing, transportation and defense industries; however, there is a need to find an environmentally- and occupationally-friendly replacement to chromate (chromium VI is considered a carcinogen with an extremely low personal exposure limit). The tasks of this stage consisted of the corrosion testing of an alternate-to- chromate coating applied to 10x3-in aluminum alloy samples, assessment of biocorrosion on aluminum alloy samples, and development and corrosion testing of a wash primer and electrophoretic coatings. The alternate to chromate coating involves substituting titanium for chromium (titanium is much safer than chromium and it is used for hip replacement in humans). The new formulation protects in the same manner as chromate and has been able to match the test data for chromated surfaces. It was found that: the conversion-coating time affects the quality and performance of the coating; wash formulations for the pretreatment of aluminum surfaces influence the adhesion of the electrophoretic coatings; and that exposure of aluminum alloy samples to suspensions of marine bacteria exhibit an increase in the corrosion rate. The report ends with a summary of future tasks to further develop chromate-free paints and anti-corrosion systems.</p>			
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INTRODUCTION

Up to now coatings containing chromate have been widely used by the manufacturing, transportation and defense industries because of chromate's effectiveness in providing corrosion resistance; however, chromium (Cr VI) has an extremely low (1 mg/m^3) personal exposure limit (PEL) (1) and is considered a carcinogen. Consequently, there has been a pressing need for the development of effective, environmentally- and occupationally-friendly coatings for corrosion protection (2 and references therein).

It has been previously reported (2) that the University of Rhode Island (URI) Corrosion Laboratory has developed a new non-chromate alternative, which contains titanium instead of chromium. The titanium formulation provides the same protection as chromate coatings and has matched test data for chromated surfaces (3). Wash primers and other chromate-free coatings need to be developed as well. A wash primer containing the electroactive polymer polyaniline was developed and corrosion tested by Yang *et al.* (4).

Because many coated surfaces are in direct contact with aqueous solutions (pipes, bridges, ships, to name a few) it is necessary to assess the effects that biofilm formation on the surfaces may have; the combined effects are known as microbially-influenced corrosion (MIC) or biocorrosion (5-6). The assessment usually involves exposure of a material sample to a microorganism suspension, followed by corrosion evaluation of the sample. Preliminary results regarding the exposure of aluminum alloy samples to a suspension of *P. atlantica* (a marine bacterium) have been reported (2).

This technical report presents the second stage results of research consisting of: corrosion testing of 10x3-in aluminum alloy panels, development of electrophoretic coatings and wash primer, and assessment of biofilm effects.

METHODS AND RESULTS

Corrosion Testing of 10x3-in Aluminum Alloy Panels

Materials

Aluminum alloy 2024 T3 was the material substrate used for all coating and biocorrosion investigations. Ten-inch long by 3-in wide, 0.032-in thick panels were obtained from Q-Panel Lab Products. This alloy does not have good corrosion resistance due to its copper content, yet it is an alloy widely used in aerospace applications due to its high strength. It is recognized as one of the more difficult alloys to protect from corrosion and as such has become an unofficial standard to use for measuring the ability of alternates-to-chromates to protect aluminum alloys.

Sample Preparation

The procedure for coating the Al 2024 T3 was a multi-step process involving degreasing, cleaning, deoxidizing, conversion coating and drying with intermediate rinsing steps in distilled water. An organic solvent was used for initial degreasing, usually acetone. Following rinsing in distilled water the panel was dipped in a commercial caustic cleaner, Turco 4215, for 5 minutes. After rinsing again in distilled water, the panel was then placed in Smut-Go, a commercial deoxidizer for 5 minutes. Following another rinse, the panel was placed in the titanate-based conversion coating. In this bath, different gases could be passed through the solution. After the conversion coating bath, the panel was given its final rinse in distilled water and left to air dry. The rationale behind using commercially available cleaners and deoxidizers was that minimal change to the accepted industrial process should be made to the conversion coating process.

Corrosion Testing

The test used to compare coating performance in this study is a salt spray test. By saturating air with a 5% by weight sodium chloride solution at 95°F, a very aggressive environment within a chamber surrounds a tray on which samples are placed. These samples are examined on a daily basis to determine any change in appearance. For Al 2024 T3, the significant changes are appearance of a white gelatinous substance from corrosion of aluminum and a red to brown color from the copper within the alloy, either of which representing corrosion of the sample.

It was noted that a ten minute conversion coating – which was the usual procedure – left a very uneven coating with poor performance, in that the coating lasted 15 days prior to corrosion at areas which were dark gray or black. One thought was that maybe the dark gray or black areas were oxidation products from copper in the alloy and if these products could be reduced, then the corrosion resistance would improve. In previous testing on 1-in wide by 4-in long by 0.032-in thick samples, these dark areas were not present and lasted 30 days in salt spray without corrosion being found. Panels of Al 2024 T3 were prepared using a nitrogen purge during conversion coating. However the performance of these panels did not improve the over that previously reported (2).

As the nitrogen purge was unsuccessful, it was decided to determine the effect of conversion-coating time on the surface appearance of the coated panels. Conversion-coating times of 1,3, or 5 minutes were used instead of the normal 10 minutes to determine if the time of

conversion coating affects the surface finish. Indeed, with shorter times, the dark areas were not present (figure 1).



FIGURE 1. 10x3- inch panel of Al 2024 T3 after conversion coating.

A comparison of the corrosion resistance related to coating appearance can be obtained by comparing figures 2 and 3 below. A coating with the dark areas after conversion coating lasts less than one day in salt spray chamber as shown in figure 2.

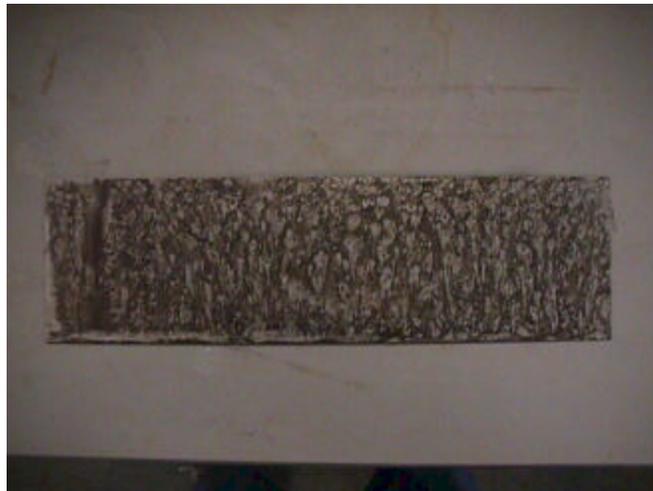


FIGURE 2. Sample with dark areas present from conversion coating after 24 hours of salt spray.

Dark areas, both as streaks and individual discrete locations can be observed on the panel, indicating poor corrosion performance. By contrast, a panel with no dark areas after conversion coating, after the same period of salt spray testing shows little dark regions, figure 3, indicating good corrosion performance.



FIGURE 3. Panel after salt spray for 24 hours, initially no dark areas were present after conversion coating.

This variation in performance with coating appearance indicates that dark areas after coating are significant to coating corrosion performance. However, they can be controlled by the time of immersion in the conversion-coating bath. It should be pointed out that a comprehensive study of conversion coating processes and coating performance measured by cyclic polarization and salt spray can be found in Guo (3).

Generally, if the coating lasts one day it will have a corrosion resistance comparable to chromates. It was shown previously (3) that over a very short time period the open circuit potential of coated Al 2024 T3 increases, indicating a protective surface was developing. This change in surface during exposure to sodium chloride solution has to occur rapidly, otherwise the opposite process to protection, corrosive attack, will occur as the Al 2024 T3 alloy corrodes if not protected in some manner. From this study it is clear that a coating with dark areas after conversion coating has a decreased performance in comparison to a coating which does not exhibit these areas.

Development of Wash Primer and Electrophoretic Coatings:

During this stage of the project, six candidate formulations for a chromate-free wash pretreatment were designed. All six formulations were tested for adhesion to metal and for their effectiveness for corrosion resistance. ASTM B117 tests were performed on 4x10-in Al 2024 panels coated with wash pretreatment alone (most panels were tested for 336 hours, some for 500 hours) and on samples coated with both the wash pretreatment and an epoxy primer overcoat (tested for 1000 hours). Control panels were chromate surface-pretreated Al 2024 panels either without or with epoxy topcoat. It was found that the performance of the wash primer is

competitive with the corresponding chromate surface pretreated samples. Both the controls and the samples pass the standard tests. Figure 4 shows a close-up photo of the scribed lines (1-mm width) after 1000 hours of salt-fog spray exposure according to the ASTM B117 standard. The images show that both the control (with chromate surface conversion) and the sample (with non-chromate wash pretreatment) performed better than passing the standard corrosion tests. There was no corrosion in the scribed area of the exposed aluminum alloy surface. This may indicate that the ingredients in the pretreatment are able to provide protection of the intentionally damaged (scribed to expose bare aluminum) area of the samples, a phenomenon referred in the literature as a self-healing coating. Since the base metal is aluminum alloy 2024, the kind of aircraft aluminum alloy most difficult to protect from corrosion, results suggest that the conducting polymer wash pretreatment is a useful replacement for the conventional chromate wash pretreatment.

A clean and shiny scratched area after salt-spray does not prove the self-healing mechanism, however. The release of the inorganic inhibitor into the aqueous phase will provide a more definitive proof and this will be explored in future research.



FIGURE 4. Photo image of scribed lines after 1000 hours of ASTM B117 salt-fog spray test. Left sample: Al 2024(non-chromate wash pretreatment)/epoxy. Right sample (control): Al 2024 (chromate surface conversion, alodine 1200)/epoxy. Note that both samples show self-healing at the scribed area.

During the tests, it was also found that one type of wash pretreatment is more efficient than the others: the best wash pretreatment contains a composite of inorganic and organic components (7). Preliminary tests show that the particles have the desirable and limited water solubility and nearly neutral pH (5-6). A particle of the composite material consists of an inorganic core (e.g. MoO_3 or CeO_2) and an organic shell (double-strand polyaniline, an electrically conductive polymer). The size of the particle ranges from 100 nm (e.g. CeO_2 :polyaniline composite) to 10 μm (e.g. MoO_3 :polyaniline composite). A transmission electron microscope picture of the nanocomposite CeO_2 :polyaniline is shown in figure 5. The advantages of this type of micro- and nanocomposites are two-fold: (a) both components of the hybrid material provide complementary and synergistic functions for corrosion inhibition, (b) the composite material can be easily formulated as additives to any commercial non-chromate wash pretreatment or primer products; it can be used as a pigment for paint.

The different formulations of the wash pretreatment of aluminum surfaces influence the adhesion to the water-borne epoxy overcoat prepared by electrophoretic coatings. One formulation showed the best performance for adhesion to the electrophoretic overcoat of epoxy. These samples were scribed to expose bare aluminum and were tested for performance in the salt-fog spray tests. It was found that the non-chromate additive provides corrosion inhibition and that the performance is competitive with chromate-conversion treated aluminum alloys.

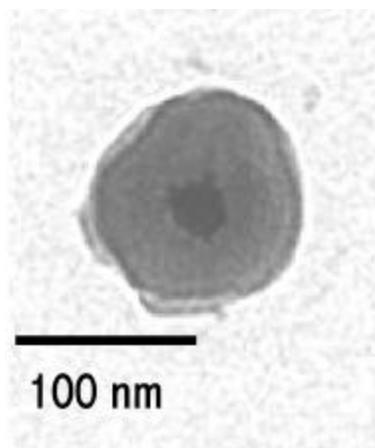


FIGURE 5. TEM image of a nano-composite of CeO_2 core with polyaniline shell. The nano particles are used as additive to the wash primer in one of the formulations developed in this research.

Assessment of Biofilm Effects (Biocorrosion)

Biofilms of *Pseudoalteromonas atlantica* were established (as described in reference 2 and in the Appendix) on bare, unpolished aluminum alloy Al 2024 T3 samples (7.6x7.6-cm).

Electrochemical impedance spectroscopy (EIS) was used to assess biocorrosion, i.e. the biofilms' contribution to corrosion (8–10). Preliminary results (2) seemed to suggest that the presence of bacteria on the alloy samples provided a resistance to corrosion as the impedance values increased with exposure time.

During this second stage of the project, the presence of bacterial biofilms on the surface of metal samples was confirmed by fluorescence microscopy and modeling of the raw EIS data by equivalent electrical circuits was accomplished.

Fluorescence Microscopy

In order to observe *P. atlantica* biofilms formed on the surface of the aluminum alloy samples, the experimental set-up has to be taken apart. The metal sample is then rinsed filtered (0.2 μm), sterile seawater to remove any loosely-attached material from the surface. Then, the bacterial biofilm is fixed with a 4-% formaldehyde solution for a couple of minutes, rinsed with filtered DI water (0.2 μm) and finally fluorescently labeled with SYBR green (Molecular Probes) for half an hour (ex. 488-nm).

Figure 6 shows *P. atlantica* growing in a one-week old biofilm formed on Al 2024; the photograph was taken using a confocal scanning (argon) laser microscope.

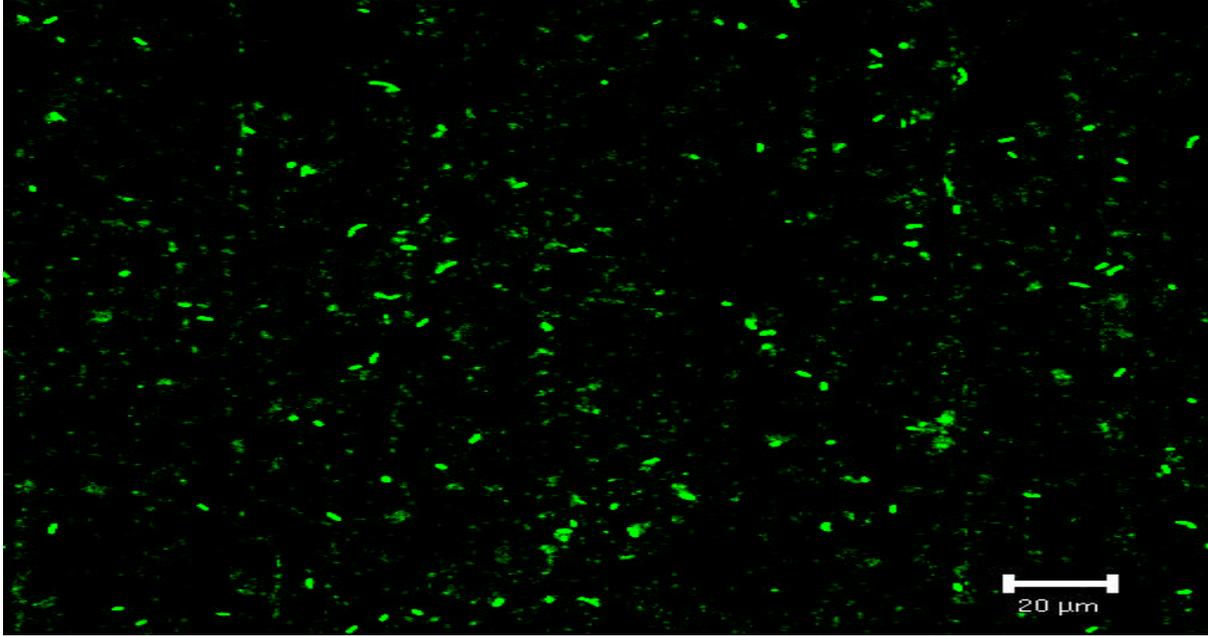
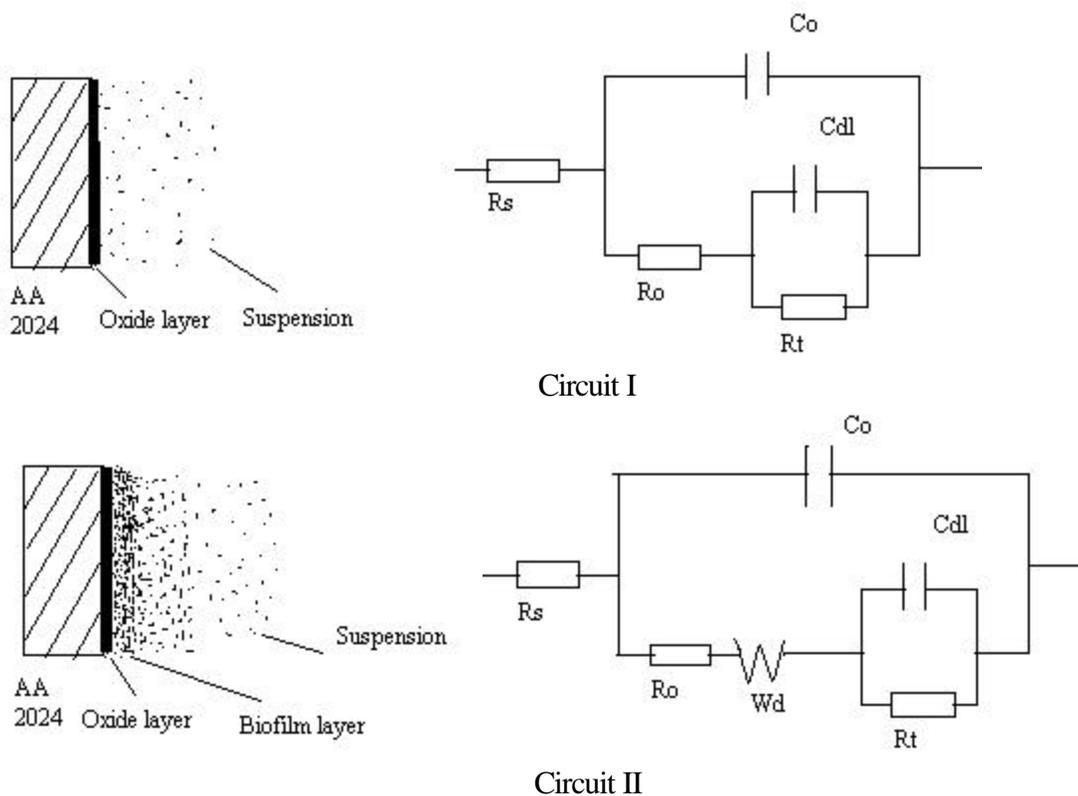


FIGURE 6. Confocal scanning laser microscope image of a one-week *P. atlantica* biofilm formed on bare Al 2024 T3.

Equivalent Circuit Modeling of EIS Raw Data

To quantify the specific contribution of the bacterial biofilm to the overall corrosion of the metal sample, modeling of the raw data (2 and Appendix) by equivalent circuits was done. Figure 7 shows the equivalent circuits for the control (bare metal samples exposed to sterile seawater) and for the biocorrosion experiment (bare metal samples exposed to the bacterial suspension). The oxide layer shown in the figure forms naturally on Al 2024 T3. The variable to focus on is R_t , the charge transfer resistance: R_t is proportional to the corrosion resistance of the metal; therefore, the higher this value the more resistance (or inhibition) to corrosion the biofilm provides.

Figure 8 shows the change in charge transfer resistance over a period of 4 weeks. The extracted data (11) show that Al 2024 T3 exposed to a bacterial suspension of *P. atlantica* has a lower charge transfer resistance as compared to the control (no bacteria in the medium); the 50% decrease in resistance is achieved at about 2 days after exposure to the bacterial suspension and remains constant throughout the duration of the experiment. A lower resistance translates into an increased corrosion rate of Al 2024 T3. This resistance decrease may be caused by extracellular acid polymers secreted by the biofilm's bacteria (12).



Rs: resistance of electrolyte Wd: Warburg diffusion impedance
 Ro: resistance of oxide layer Co: capacitance of oxide layer
 Rt: charge transfer resistance Cdl: capacitance of double layer

FIGURE 7. Equivalent circuits of the impedance spectra: circuit I for aluminum alloy 2024 T3 exposed to suspension without *P. atlantica* (control); circuit II for aluminum alloy 2024 T3 exposed to a *P. atlantica* suspension.

Other Experimental Observations

Metal Sample Sterilization: Initially the assembled experimental set-ups were sterilized by autoclaving for 20 minutes at 121 °C previous to initiating the experiments (2). It became obvious that autoclaving resulted in corrosion of the metal sample (it was mentioned above that Al 2024 T3 is very susceptible to corrosion due to its high copper content (4%). It was decided then to sterilize the whole set-up overnight with UV light in a laminar-flow hood.

Switch from aluminum alloy 2024 T3 to 3105: Because of the same reason, high copper content, it was decided to conduct future experiments with aluminum alloy 3105 (0.3% copper content); this will minimize any corrosion which may result from the sample preparation steps.

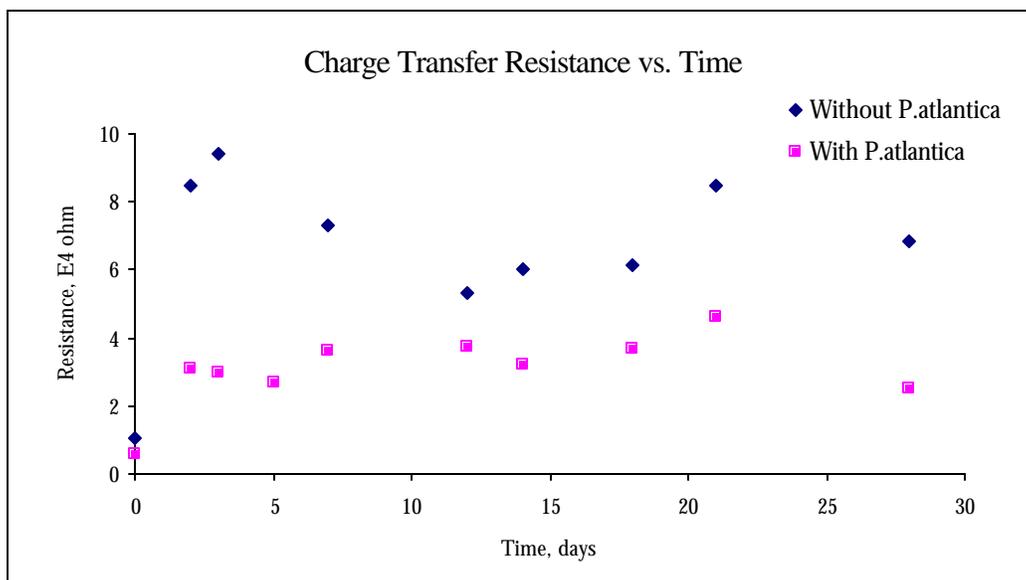


FIGURE 8. Charge transfer resistance as a function of time.

CONCLUSIONS

1. The conversion-coating time affects the quality and the performance of the coating. Longer times result in a more uneven surface and poor anticorrosion protection of the coating.
2. Different wash formulations for the pretreatment of aluminum surfaces influence the adhesion to the water-borne epoxy overcoat prepared by electrophoretic coatings. One formulation showed the best performance for adhesion to the electrophoretic overcoat of epoxy. It was found that the non-chromate additive provides corrosion inhibition and that the performance is competitive with chromate-conversion treated aluminum alloys.
3. Uncoated aluminum alloy Al 2024 T3 samples show increased corrosion rate when exposed to suspensions of marine bacteria (*P. atlantica*).

FUTURE WORK

The present work represents the second phase of a multi-year project. The principal tasks for the coming years are:

1. To decrease the conversion coating time to optimize the corrosion resistance of the coating.
2. To assess biocorrosion of bare and coated metal samples exposed to nutrient-poor bacterial suspensions.
3. Design composites with a range of inhibitor release rates.
4. Test the storage/release rate of pigments when incorporated in the wash primer coating.

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APPENDIX

This appendix contains information about the experimental protocols used in the biocorrosion experiments, as reported in reference 2 of the main manuscript. It also contains information about publications and presentations related to this project.

Biocorrosion Experiments Protocol (2)

Bacterial cultures

Cultures of a marine bacterium, *Pseudomonas fluorescences* (ATTC 43666), were established and later used in (MIC) experiments. Briefly, *P. atlantica* is streaked from a – 75°C glycerol stock onto an agar plate. A single colony is then picked and used to inoculate 5 mL of sterile Zobell 2166 medium (5 g/L peptone, 1 g/L yeast extract, filtered seawater) without shaking at 19 °C. After two days the inoculum is transferred into larger Erlenmeyer flasks kept at 19 °C. Once the bacterial suspension reaches a cell density of at least 10⁶ cells/mL, it is used for MIC experiments.

Biocorrosion Experiments

Biocorrosion experiments on uncoated aluminum alloy Al 2024 T3 samples were initiated. Steps involved are as follows:

Metal Sample Preparation: Bare, unpolished aluminum 2024 T3 square samples (7.6x7.6-cm) were degreased and cleaned with DI water, acetone and alcohol, air-dried in a laminar-flood hood and sterilized by UV light overnight before each experiment.

Experimental Set-up: The experimental set-up (figure A.1) consists of a 4-cm diameter, open-ends glass tube clamped to an aluminum alloy sample; this results in a 12.6-cm² exposed metal surface area to the bacterial suspension. An ethylene propylene O-ring is used to create a watertight seal. After assembly, the set-up is sterilized by autoclaving at 121 °C for 20 minutes before initiating the experiments.

Experiments and Assessment of Biocorrosion: Biocorrosion experiments were conducted in duplicate set-ups containing 200 mL of medium with or without bacteria (control) at 19°C for one month. Electrochemical impedance spectroscopy (EIS) was used to assess the biofilm's contribution to corrosion. Typical raw data obtained from the experiment are shown in figure A.2.

Publications and Presentations

1. Tang, Z., N. Alvarez and S. C. Yang (2002). Organic/Inorganic Hybrid Material for Coating on Metals. Materials Research Society Symposium Proceedings (Polymer/Metal Interfaces and Defect Mediated Phenomena in Ordered Polymers), pp. 357-363.

- Cai, H., R. Brown and M. A. Rivero-Hudec (2003). Effect of *Pseudoalteromonas atlantica* on the Corrosion of Aluminum Alloy 2024. Accepted for presentation at the General Corrosion Poster Session, 204th Meeting of the Electrochemical Society, October 2003.



FIGURE A.1. Biocorrosion experimental set-up.

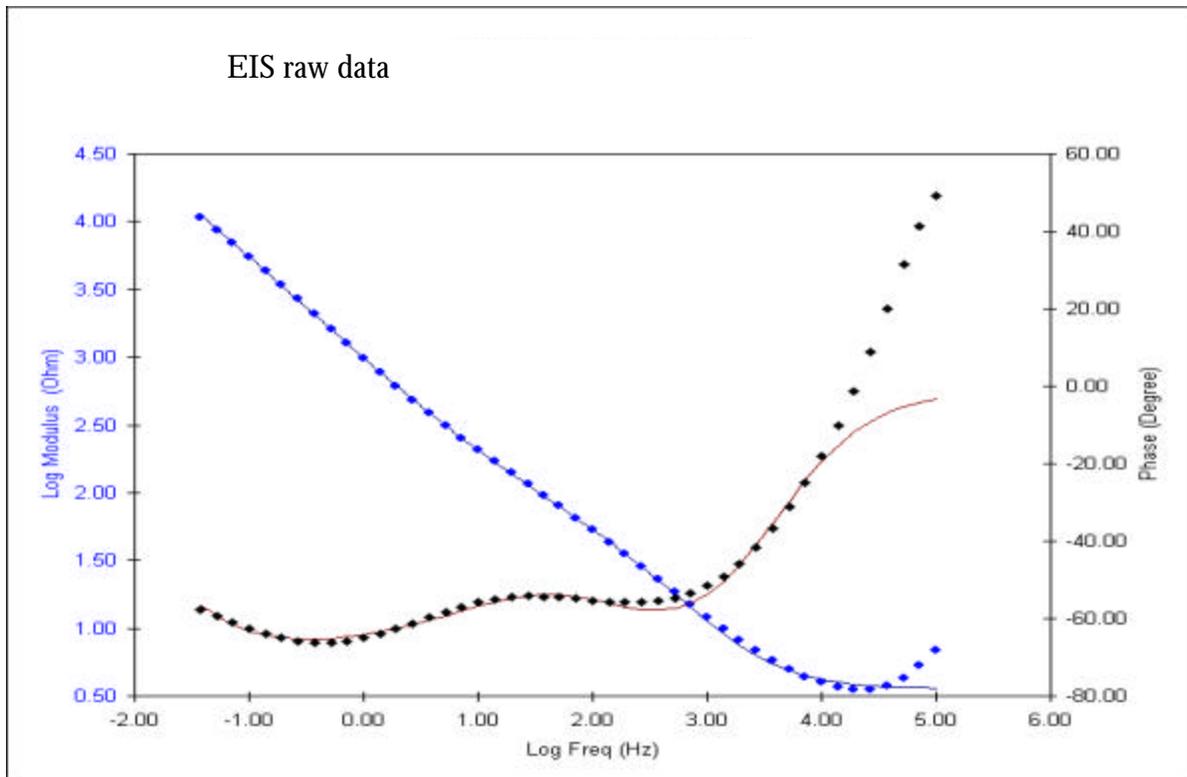


FIGURE A.2. EIS raw data.